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# Effects of alkyl substitution on the physical properties and gas transport behavior in selected poly(R-phenoxyphosphazenes)

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# ABSTRACT

A systematic preparation of alkyl substituted phenoxyphosphazene polymers was performed and their gas transport properties determined. In this study, phosphazenes substituted with 4-methylphenol, 4-ethylphenol, and 4-isopropylphenol are reported. An additional polymer substituted with 4-tertbutylphenoxy-1-ethanol also was synthesized in this work. Data derived for these materials, including chemical, thermal and gas transport characterization, were compared to previous reports discussing poly [bis-phenoxyphosphazene] and its analog with tert-butyl substitution: poly[bis-(4-tert-butylphenoxy) phosphazene]. The tert-butyl moiety influences orderly chain packing, presumably through steric hindrance that can influence aromatic  $\pi$ -stacking. For the new poly[(alkylphenoxy)phosphazene], semicrystallinity is maintained and the added steric bulk serves to decrease the polymer glass transition temperature (Tg) and increase both permeability and selectivity for the gas pairs:  $O_2/N_2$  and  $CO_2/CH_4$ . Removal of the tert-butyl moiety from the immediate vicinity of the backbone through a flexible spacer serves to depress the Tg as compared to poly[bis-(4-tert-butylphenoxy)phosphazene], but provides no performance enhancement for gas transport.

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#### 1. Introduction

Poly(organophosphazenes) are unique materials that are composed of an alternating phosphorus and nitrogen backbone. Tethered to the phosphorus are pendant groups that serve to stabilize the polymer to hydrolysis and provide variation in the polymers' chemical and physical properties [1]. Phosphazenes are of interest due to their high degree of chemical stability. Many phosphazenes can be considered high performance polymers in that they are stable at temperatures as high as 300 °C [2]. The synthesis of poly(organophosphazenes) differs from that of other polymers in that the backbone is formed initially, followed by a substitution process to yield the final material from which membranes can be formed [reference needed]. In our laboratories, the polymer backbone is formed by ring-opening polymerization of commercially available hexachlorocyclotriphosphazene, 1, to yield linear poly[bischlorophosphazene], 2, Fig. 1. Poly(bis-chlorophosphazene) is an unstable material when exposed to ambient moisture due to the lability of chlorine. Exposure to moisture leads to nucleophilic attack by water at the phosphorus resulting in evolved HCl and the

formation of phosphorus-oxygen bonds (P–OH, P=O), which themselves result in backbone cleavage through hydrolysis of P–N bonds. The key to stabilization of the polymer is removal of chlorine and replacement with nucleophiles, such as alcohols [3], amines [4], or organometallic reagents [5], as represented by structure **3**. Numerous substitution chemistries have been reported [6].

The unique chemistry of polyphosphazenes allows for a systematic study of structure using standard analytical techniques, and through applications, such as gas transport. Through controlled pendant group substitution, a strategic approach to polymer composition can be made. An example of this concept is the balance between hydrophilic and hydrophobic groups and the resultant effect on gas permeation [7]. Hydrophilicity was provided by 2-(2-methoxyethoxy)ethanol (MEE) and the hydrophobic component was 4-methoxyphenol. Increased permeability for CO<sub>2</sub> was observed with increased MEE substitution, which was attributed to an affinity between MEE and the permeant gas. A refinement of this study showed that the relationship was more likely due to a correlation with the polymer glass transition temperature (Tg), where lower Tg polymers, regardless of chemical functionality, yielded higher CO<sub>2</sub> permeability [8]. Another example examined polyphosphazenes formed with phenol and 4-phenylphenol pendant groups at various loadings of each [9]. In this series, the range of Tg values obtained was not as wide; however, the same





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Fig. 1. Synthesis of stable poly(organophosphazenes).

general relationship between increased gas permeation with decreasing Tg was observed.

In this paper, a series of polymers were formed with potential constraint of backbone motions, through the systematic attachment of bulky groups to phenoxy-substituted polyphosphazenes, and the effect of this substitution on gas permeability was explored. Discussed are phosphazenes formed with 4-methylphenol, 4ethylphenol, and 4-isopropylphenol pendant groups. Selection of these polymers builds upon previous work characterizing the gas permeability of poly[bis-phenoxyphosphazene], 4 and poly[bis-(4tert-butylphenoxy)phosphazene], 5 [10]. The new alkylphenoxyphosphazene polymers in this work were selected to span the range defined by 4 and 5 in terms of steric bulk at the para position of the aromatic ring. An additional polymer was synthesized as a part of this study that displaced the substituted alkylphenoxy moiety farther from the polymer backbone through an ethyleneoxy spacer, **11**, Fig. 3. All polymers will be discussed in terms of how the alkyl substitution at the 4-position (para) affects properties, such as Tg and the gas permeability for selected gases (H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>.)

# 2. Experimental section

#### 2.1. Methods and materials

Hexachlorocyclotriphosphazene was purchased from Aldrich Chemical Company and Esprit Chemical Company and sublimed in vacuo at 85 °C prior to use. Anhydrous solvents (toluene, tetrahydrofuran (THF), and 2-methoxyethylether), 4-methylphenol, 4ethylphenol, 4-isopropylphenol, ethylene glycol, *p*-toluene sulfonyl chloride, silica gel (200-400 mesh), and sodium hydride (as a 60% dispersion in mineral oil), also were acquired from Aldrich Chemical Co. and used as received. Methanol, ethyl acetate, and hexane were purchased from VWR and used without purification. Polymer 4 was acquired from Elf-Atochem and used as received. Nuclear magnetic resonance (NMR) spectra were collected using a Bruker DMX 300 WB operating at 7.04 T field strength: 300 MHz (<sup>1</sup>H) and 121 MHz (<sup>31</sup>P). <sup>31</sup>P chemical shifts were referenced to an external H<sub>3</sub>PO<sub>4</sub> standard. Thermal characterization data were acquired using a TA Instruments model Q200 differential scanning calorimeter (DSC) and a model Q500 thermogravimetric analyzer (TGA). Polymer densities were obtained by helium pycnometry using a Micromeritics Accupyc Model 1330 pycnometer. Molecular weight determinations were performed using Gel Permeation Chromatography against polystyrene standards by Polyhedron Laboratories, Inc. (Houston, TX).

#### 2.2. Synthesis of poly[bis-chlorophosphazene] (2)

Synthesis of poly(bis-chlorophosphazene), **2**, which was synthesized by ring-opening melt polymerization at 250 °C using a modified method of Singler [11]. Into a thick-walled glass tube was added hexachlorocyclotriphosphazene, **1** (60 g, 172 mmol). The tube was sealed under vacuum and heated in an oven at 250 °C until flow was nearly absent. Time varies depending on the source of **1**, which can vary between 12 and 60 h. Crude polymer was separated by dissolution of the resulting opaque white rubber into 75 ml of toluene followed by precipitation into 800 ml of hexane. The desired rubber was obtained by decanting off unreacted **1**. Polymer **2** was not isolated. To minimize decomposition or unwanted cross-linking of this material, it was immediately dissolved into dry toluene and used within a day.

# 2.3. Poly(bis- phenoxy)phosphazene (4) and poly[bis-(4-tertbutylphenoxy)phosphazene] (5)

The synthesis and characterization of polymers **4** and **5** have been reported elsewhere [10].

# 2.4. Synthesis of the poly[(4-alkylphenoxy)phosphazenes] (6–8)

Polymers 6–8 were synthesized using a similar method. The synthesis of polymer 6 is shown here. In a three neck 2 L round bottom flask was added a thermometer, mechanical stirrer, nitrogen purge, a heating mantle, and a condenser. To this was added 34.67 g (321 mmol) of 4-methylphenol followed by  $\sim$  300 ml of anhydrous THF. To this mixture was added sodium hydride (12.84 g, 321 mmol) in small increments under a nitrogen purge. Once all of the hydride was added, the reaction was allowed to stir for 1 h to ensure complete reaction. Poly[bischlorophosphazene] (9.31 g, 80 mmol), as a solution in 75 ml of anhydrous toluene, was added to the reaction mixture. To this mixture was added ~200 ml of anhydrous 2-methoxyethylether and the temperature was increased to 105 °C. To attain this temperature, a Dean-Stark adapter was added to the experimental apparatus to remove lower boiling THF until the temperature reached 105 °C. This reaction was monitored by <sup>31</sup>P NMR until no further changes in the spectra were noted, approximately 4 days. The reaction was cooled to room temperature. Isolation of the polymer was accomplished by successive precipitations from THF solution (300-500 ml). Initially, the mother liquor was poured into a mixture of ethanol/water (2250 ml/250 ml) and the polymer was collected. The second precipitation was into deionized water (3 L) and the third was into hexane (1 L). The final polymer mass was collected and dried in a vacuum oven at 65 °C overnight. Polymer 6: yield 86%. Polymer 7: yield 68%. Polymer 8: yield 43%.

# 2.5. Ethylene glycol monotosylate, 9

A dry 2 L 3-necked round bottom flask was charged with ethylene glycol (853 g, 13.75 mol), triethylamine (75.7 g, 550 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), (1 ml, 6.7 mmol). The resulting mixture was stirred at 0 °C in a water ice bath. The flask was then equipped with an addition funnel charged with *p*-toluenesulfonyl chloride (53.8 g, 275 mmol) in methylene chloride (400 ml), which was added to the reaction flask slowly over 2 h. The final reaction mixture was allowed to come to room temperature and was stirred overnight. The reaction mixture was then transferred to a 2-L separatory funnel and was washed with two 200 ml portions of saturated NaHCO<sub>3</sub>, two 200 ml portions of saturated NaCl. The remaining organic was stripped of methylene chloride to yield

a pale yellow oil, 34.7 g. The oil was characterized by NMR spectroscopy to be a mixture of the desired product, ethylene glycol monotosylate, 91%, with remainder consisting of ethylene glycol ditosylate. No separation of this mixture was performed.

# 2.6. 2-(4-Tert-butylphenoxy)-1-ethanol, 10

A dry 1 L 3-neck round bottom flask was charged with tertbutylphenol (26.0 g, 173 mmol), anhydrous toluene (100 ml) and anhydrous 1,4-dioxane (600 ml). To this was added a magnetic stirbar and a dry N<sub>2</sub> sparge gas. Sodium hydride (3.98 g, 173 mmol) was added slowly and the resulting mixture was stirred until no evidence of hydrogen evolution was observed. In a second flask, an oven dried 2 L 3-neck, a solution was formed from 9 in toluene (50 ml) and anhydrous 1,4-dioxane (500 ml). The contents of the first flask were then added slowly over 45 min to the second. The reaction was then heated to reflux for 3 h upon which a large amount of white precipitate formed. The reaction was cooled and filtered. The filtrate was washed with two 200 ml portions of water and then the organic layer was dried with anhydrous MgSO<sub>4</sub>. Stripping of the solvent by rotary evaporation yielded 27.8 g of crude product. NMR analysis showed the desired 2-(4-tert-butylphenoxy)-1-ethanol, 10, along with ethylene glycol di-tertbutylphenoxide, and a small amount of *p*-toluenesulfonic acid. The acid was removed by dissolution of the crude product in hexane, followed by filtration. The filtrate was then stripped of solvent and chromatographed on a silica gel column using a mixture of 70% hexane/30% ethyl acetate as the eluent. Collection of the desired fraction from the column yielded **10** as an oil (7.8 g, 15% yield from *p*-toluenesulfonyl chloride).

# 2.7. Poly(bis-(2-(4-tert-butylphenoxy)-1-ethoxy))phosphazene, 11

To a dry 1 L 3-necked flask, equipped with a mechanical stirrer, thermometer, and nitrogen purge, was added **10** (15.3 g, 78.9 mmol) and anhydrous THF (300 ml). Sodium hydride (2.87 g, 74.9 mmol) was added over 10 min and the resulting solution was stirred for 1 h at room temperature. At this time, a solution of polymer **2** in anhydrous toluene (70 ml) was added to the reaction mixture and the resulting solution was stirred at room temperature for 20 h, at which time it was determined to be complete by P-31 NMR spectroscopy. Isolation of the product polymer was performed by pouring the mother liquor into 2.5 L of 80% isopropanol in water. The polymer floated on top of the solution and was mechanically collected. This material was then dissolved into THF (200 ml) and precipitated into water (1.5 L). The collected swollen rubber was redissolved into THF (200 ml) and centrifuged to remove any undissolved matter. The clarified solutions were then poured into methanol (1 L) and the collected precipitate was dried in a vacuum oven at 60 °C. Drying yielded 6.5 g of an off-white rubber in 76% vield.

# 2.8. Membrane formation

Membranes were formed using a solution casting method from THF at polymer concentrations ranging from 2 to 8% by weight. After dissolution, the solutions were clarified by centrifugation to remove insoluble material, if necessary. In a fume hood, stainless steel supports with a 0.5 pore diameter were placed on a level surface and the polymer solutions were cast directly using a Pasteur pipette. The membranes were covered with a beaker to slow the evaporation rate for the best results in forming defect free membrane films. After several hours, additional membrane drying was performed in an oven at 60 °C. Previous work has shown that membranes formed in this method using high molecular weight phosphazenes (>100 kD) result in no significant intrusion of the polymer into the support. Characterization of thickness was determined using two methods. First, thickness was calculated by measurement of the mass of polymer applied to the support and the polymer density. Second, measurement of thickness was also performed using a micrometer, which upon subtraction of the support thickness, yielded values consistent with the calculation method. Thicknesses ranged from 20 to 80  $\mu$ m. The strong correlation between these two methods suggested that intrusion of the polymer into the pores of the support was minimal.

# 2.9. Pure gas permeability analysis

Permeabilities were determined using a literature barometric method [12,13] where the permeate volume was 1021.5 ml, the membrane area was 13.2 cm<sup>2</sup>, and the initial feed gas pressure was 30 psi. Gases studied included H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>.

# 3. Results and discussion

# 3.1. Synthesis of alkoxyphenoxy phosphazenes

Synthesis of polymers 6-8 was performed by exposure of previously prepared poly[bis-chlorophosphazene], 2, with nucleophiles, themselves formed from the reaction of commercially available phenols with sodium hydride. The reactions were monitored regularly using <sup>31</sup>P NMR spectroscopy performed on small aliquots removed from solution. In general, at the beginning of the reaction, polymer **2** gives a strong narrow singlet at approximately -19 ppm. Upon the addition of aromatic nucleophiles, multiple peaks are seen to form approximately -15 ppm. As the reaction progresses, a peak corresponding to the desired homogeneously substituted structures grows in at approximately -17 ppm. Near completion, only one peak is observed and the width narrows as the remaining chlorines are displaced. Once complete, the product polymer is isolated and purified through a series of precipitations into selected solvents. Removal of entrained solvent yields solid materials whose physical characteristics are largely dictated by the pendant group. Poly[bis-phenoxyphosphazene], 4, is a fibrous solid. Use of 4-methylphenol as a pendant group results in little gross change to the polymer, as does the use of 4ethylphenol. Polymer 8 with 4-isopropylphenol substitution does yield a significant change. This polymer was dense rubbery solid. Interestingly, polymer 5, poly[bis(4-tert-butylphenoxy)phosphazene] tends to be somewhat fibrous.

As a probe of the dependence of the location of the tert-butyl group with respect to the polymer backbone, polymer **11**, Fig. 3, was prepared. The pendant group for this polymer is not available commercially and was prepared in our laboratories, Scheme 1. Initially, one hydroxyl moiety on ethylene glycol was converted to the tosylate using a large excess of ethylene glycol to minimize attachment of tosylate at both hydroxyl positions. Selectivity of up to 92% monotosylate addition has been achieved. Attachment of 4-tert-butylphenol was achieved through a Williamson ether synthesis by reaction of the phenol with sodium hydride, followed by exposure to the ethylene glycol monotosylate. Please note that the di-substituted tosylate was not removed before 4-tert-butylphenol attachment, so allowances were made in the addition of the phenoxide to account for the equally reactive and undesired disubstituted adduct.

Purification of the desired compound, **10**, was performed using silica gel column chromatography. Attachment of **10** to polymer **2** proceeded similarly to the previously discussed polymers **6–8**, yielding polymer **11**. The net effect of the chemistries was to insert an ethyleneoxy  $(-CH_2-CH_2-O-)$  linkage between the polymer



**Scheme 1.** Synthesis of 2-(4-tert-butylphenoxy)-1-ethanol.

backbone and the 4-tert-butylphenol. The effect on gross properties was substantial, where the product was a dense rubber.

# 3.2. Thermal characterization and pycnometry

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were employed to probe the morphology and stability of the polymers. Data is shown in Table 1. A previous report from our laboratory discussed polyphosphazenes substituted with phenol, **4** and 4-tert-butylphenol, **5** [10]. The difference between these polymers was the substitution at the para position, proton versus a tert-butyl group, Fig. 2. Poly[bis-phenoxyphosphazene], 4, is a semicrystalline polymer [14,15]. Cast directly from solvent yields a membrane that is approximately 45% crystalline; although the degree of crystallinity is heavily influenced by thermal history [16]. Crystalline domains may be attributable to aromatic  $\pi - \pi$ interactions that serve to create order in the system. Attachment of the tert-butyl groups at the para position can somewhat, but not completely, disrupt the  $\pi - \pi$  interactions, therefore changing the morphology of the polymer. The Tg values for polymers 4 and 5 are available in the literature at -1 °C and 43 °C, respectively [10]. In

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Thermal	analysis	and	pycnometry	data.

Table 1

Polymer	Tg (°C)	$T_1$ (°C)	)	$T_{\rm d}$ (°C)	Density (g/cm <sup>3</sup> )	Ref
4	-1	99	126	351	1.332	[10]
5	48	118		386	1.160	This work
6	-0.6	134	156	388	1.223	This work
7	-18	54	101	334	1.202	This work
8	-19	47	69	398	1.140	This work
11	23	None		327	1.126	This work

this work, a Tg of 48 °C was measured for polymer **5**. Most important is the observation of a  $T_1$  transition associated with crystalline rearrangement at 118 °C, somewhat lower than recorded by Bowmer [17] (140 °C). The higher Tg of **5** also suggests the substituent has a hindering influence on backbone chain flexibility.

Methyl substituted polymer **6** has nearly the same Tg as **4** at -0.6 °C; however, the  $T_1$  transitions are significantly higher in temperature. It can be concluded that a methyl group is not large enough to significantly influence the backbone mobility, nor does it significantly disrupt crystallinity, which is not surprising considering the data for **5**. The slightly larger ethyl substituent on polymer **7** does influence the Tg as shown in a decrease to -18 °C, consistent with Bowmer [17], which is due to the flexible nature of an ethyl group and its ability to self-plasticize the polymer structure. Crystalline transitions are also seen with this polymer, but the temperatures at which they are observed are lower than polymer **4**. Isopropyl substitution, polymer **8**, does not result in a further loss in Tg, where it was measured at -19 °C and the semicrystalline nature remained; however, the transitions were significantly lower in temperature than what was observed for polymer **7**.

Placement of the ethyleneoxy spacer moves the tert-butyl group farther from the polymer backbone, thus lessening its influence on backbone motion. The Tg for polymer **11** (Fig. 3) was 23 °C which suggests that the backbone motional freedom is influenced by the highly flexible ethyleneoxy structures, which counteracts the hindering influences of the tert-butyl groups. A complete absence of semicrystallinity is observed for this polymer.

TGA of the polymers using air as the purge gas suggests little effect on the overall polymer stability with respect to temperature. The four polymers with aromatic moieties directly attached to P had decomposition temperature ( $T_d$ ) values similar to each other. The outlier was polymer **11**, with a  $T_d$  substantially lower, which is



Fig. 2. Structures for (poly)organophosphazenes 4-8.

attributable to the lower thermal stability seen in polymers with ethereal linkages attached to P. This conclusion is consistent with poly[(bis-(2-(2-methoxyethoxy)ethoxy))phosphazene], formed with 100% MEE substitution, which decomposes at 280 °C [18].

Pycnometry was used to measure the densities of the various polymers. In our previous report, we were able to reflect upon the observation that the attachment of tert-butyl groups resulted in lower polymer density [10]. This seemed reasonable due to the steric influences of these groups. In this study, the incremental attachment of alkyl groups serves to incrementally lower the polymer densities giving the following order:  $4 > 6 > 7 > 8 \approx 5$ . Please note that the data derived from isopropyl and tert-butyl attachments result in little difference. The density for **11** was the lowest of the set in this paper, which may be a reflection of the fact



Fig. 3. Structure of polymer 11.

that this polymer has the highest organic fraction as a function of overall polymer structure.

# 3.3. Dilute solution characterization

In an attempt to further understand the gross physical properties of the polymers, dilute solution Gel Permeation Chromatographic analysis was performed. The lack of control in the polymerization of hexachlorocyclotriphosphazene, **1**, has been discussed extensively [19]. The rate and degree of polymerization of **1** are susceptible to multiple influences including inorganic impurities, water, oxygen, as well as the presence of Lewis acids such as the boron contained in the borosilicate glass polymerization tubes. Table 2 shows the data for the six polymers in this study. Direct comparison of the data must consider the use of differing supplies of hexachlorocyclotriphosphazene, **1**; poly [bis-chlorophosphazene], **2**; and analysis methods. Data for polymer **4** was provided by the supplier and **5** comes from a previous report [10]. Polymers **6–8** and **11** discussed in this work were studied by an outside vendor.

Table 2
Gel permeation chromatography characterization data

Polymer	Mw (Daltons)	Polydispersity Index (PDI)	Ref
4	$6.00 \times 10^{5}$	NA	[10]
5	$1.15  imes 10^6$	1.14	[10]
6	$3.68  imes 10^5$	38.8	This work
7	$3.77  imes 10^5$	16.6	This work
8	$3.73  imes 10^5$	10.0	This work
11	$7.79\times10^5$	22.4	This work

Other differences include the fact that polymer **11** and polymers **6–8** were formed using differing batches of polymer **2**, and these batches were formed from hexachlorocyclotriphosphazene supplied by differing vendors. The importance of these molecular weight and PDI differences on characteristics such as thermal transitions and gas transport is a fact that should be examined. Polymer **4** offers the best opportunity to study these effects due to the wealth of information available in the literature [10,16,20,21]. A comparison of data reveals little deviation in permanent gas permeability and Tg, although it could be argued that molecular weight would critically influence gross mechanical behaviors, such as stress/strain and tensile strength.

# 3.4. NMR characterization

NMR characterization of phosphazenes typically employs the commonly observed <sup>31</sup>P, <sup>1</sup>H, and <sup>13</sup>C nuclei. Observed atoms are more sensitive to changes in their immediate vicinities than they are with more remote structures. For example, single <sup>31</sup>P peaks were observed for all four new polymers, Table 3. Polymers 6, 7, and **8** all have roughly similar chemical shifts (approximately -17to -8 ppm), which is not unreasonable. In fact, this compares well to polymers 4 and 5. Modifications in 6-8 were performed relatively far from the polymer backbone, thus the influence of the alkyl substitution on the aromatic rings is minimal as seen at phosphorus. Polymer 11 also supports this assertion. Insertion of the ethyleneoxy spacer group at phosphorus directly influences the phosphorus chemical shift. A singlet is seen at -6.2 ppm, which is consistent with other phosphazenes that have ethyleneoxy substitution at phosphorus [22]. Proton and <sup>13</sup>C NMR spectroscopy were used to confirm the presence and structure of the organic components of the polymers, Table 3.

#### 3.5. Pure gas permeability and ideal selectivity

Phosphazenes have been studied as membranes for gas separations [23,24]. To characterize this set of phosphazenes, pure gas permeability measurements were obtained from flat sheet membranes at 30 °C. Gases used in this study included H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> and a data summary for these gases is shown in Table 4. This selection of gases represents an envelope of gas properties, which dictate the relative contributions of diffusion and solubility to the mechanism of gas transport. The envelope spans from small highly penetrating gases (H<sub>2</sub>) to larger more condensable gases (CO<sub>2</sub>).

Permeability of any gas i through a membrane has been described as a function of the gases' solubility (*S*) in the membrane and it ability to diffuse (*D*) through the membrane, Eq. (1) [25].

$$P_i = D_i \times S_i \tag{1}$$

An equally valuable term is the ideal gas selectivity,  $\alpha$ , which is defined as a ratio of the pure gas permeability measurements for

Table 3

NMR characterization data.						
Polyme	er <sup>31</sup> P (ppm)	<sup>1</sup> H (ppm)	<sup>13</sup> C (ppm)			
6	-18.1	6.74 (d), 6.58 (d), 2.10 (s)	150.1, 132.7, 129.6, 121.5, 21.1			
7	-17.5	6.79 (d), 6.60 (d), 2.38 (dd), 1.05 (dd)	150.2, 139.1, 128.4, 121.7, 28.6, 16.0			
8	-17.4	6.79 (d), 6.63 (d), 2.61 (m), 1.03 (d)	150.3, 143.7, 126.9, 121.8, 33.8, 24.5			
11	-6.2	6.99 (d), 6.56 (d), 4.34 (brs), 3.89 (brs), 1.14 (s)	156.9, 143.3, 126.5, 114.5, 67.7, 65.2, 34.4, 32.0			

# Table 4

Pure gas permeability data. Permeability given in Barrers (1 Barrer =  $1.33\times 10^4~m^2(STP)~m~m^{-2}~s^{-1}~kPa^{-1}).$ 

Polymer	Permea	Permeability (Barrers)				Ref
	H <sub>2</sub>	CO <sub>2</sub>	02	$N_2$	CH <sub>4</sub>	
4	7.5	4.8	2.1	1.3	1.2	[10]
5	23.0	17.0	8.2	2.4	1.7	[10]
6	9.3	10.2	3.4	1.1	2.8	This work
7	21.3	32.3	15.0	4.9	8.9	This work
8	98.2	135.1	41.6	14.2	30.3	This work
11	16.2	13.8	3.5	0.9	1.7	This work

gases i and j. Further, this ideal selectivity can be described as a function of the solubility selectivity and the diffusivity selectivity, Eq. (2).

$$\alpha_{(i,j)} = (P_i/P_j) = (D_i/D_j) \times (S_i/S_j)$$
<sup>(2)</sup>

Hydrogen is a small gas whose transport is largely diffusive. A previous report has discussed H<sub>2</sub> permeation through **4** and **5** [10]. Upon attachment of the tert-butyl group, the H<sub>2</sub> permeability modestly, but significantly, increased from 7.5 Barrers for **4** to 23 Barrers for **5**. If we assume that **4** and **5** represent extremes and that **6**–**8** are incremental changes between these extremes, then their H<sub>2</sub> permeabilities would be expected to be between 7.5 and 23 Barrers. Polymer **6** permeability measured 9.3 Barrers, consistent with the expectation. However, polymers **7** and **8** did not follow the expected trend. H<sub>2</sub> permeability for ethyl substituted **7** was significantly larger than **6**, and almost as large as **5**, at 21.3 Barrers. Isopropyl substituted polymer **8** gave an even more unexpected H<sub>2</sub> permeability of 98.2 Barrers.

Previous reports have demonstrated the relationship between polymer Tg and gas permeability [8]. In general, lower Tg values result in higher gas permeabilities. This relationship has been demonstrated with CO<sub>2</sub>; however, it remains applicable, although to a lesser degree, to the other gases in this study. The isopropyl group performs an internal plasticization role, resulting in a far lower Tg than expected. The lower Tg, which correlates to higher polymer segmental chain motions, may also result in higher gas permeability. However, this rather simple correlation is not universal as shown by the comparison of **5** and **11**. In **11**, the sterically bulky tert-butyl group is more remote from the backbone, thus exhibiting less hindrance on chain motions as reflected by a lower Tg than **5**. However, the lower Tg does not result in higher H<sub>2</sub> permeability. It is significantly less suggesting other influences such as gas solubility may play a role.

Highly condensable gases, such as CO<sub>2</sub>, exhibit more solubility driven permeability in many membrane separations [26]. Polymer **4** shows the lowest CO<sub>2</sub> permeability at 4.8 Barrers. The tert-butyl group raises the permeability to 17.0 Barrers. Once again, the methyl group substituted polymer **6** was found inside the limits established between **4** and **5** at 10.2 Barrers. However, **7** and **8** were substantially higher at 32.3 and 135.1 Barrers, respectively. This data supports both diffusivity and solubility contributions to transport. Using a diffusive argument, the Tg values for both **7** and **8** are much lower than **6**, which explains significantly higher permeability values with respect to the unsubstituted polymer **4**. However, the significant permeability difference between **7** and **8** cannot be explained by a Tg argument alone due to their similarity. However, the difference in CO<sub>2</sub> permeabilities may be a function of solubility influences induced by the additional alkyl content of **8**.

Ideal gas selectivity is a relative measure of the membrane's ability to perform an actual gas separation. In the determination of an ideal separation factor, the nature of each gas and the polymer membrane dictate the behavior and provides a probe of structure



Fig. 4. Permeability/selectivity plot for O<sub>2</sub>/N<sub>2</sub>.

necessary to create membrane materials with both higher permeability and selectivity. Robeson reported in 1991 an empirical correlation between the permeability and ideal selectivity of a membrane towards selected gas pairs [27]. The result of this work is an easily employed method to assess membrane performance. An inverse correlation, or trade-off, in membrane performance is observed for many membranes. This observation reflected the common occurrence in which an increase in the permeability of a selected gas component often results in a loss in selectivity. Graphically, this observation was shown as an empirical upper bound on membrane performance. The Robeson upper bound has become a useful measure to compare membrane performance and to judge the results of either material or process modifications to membrane systems. In 2008, Robeson updated the empirical correlation to reflect the abundance of new membrane materials



Fig. 5. Permeability/selectivity plot for CO<sub>2</sub>/CH<sub>4</sub>.

and processes that increased the upper bound to higher levels for many gas pairs [28].

Application of the upper bound analysis to the  $O_2/N_2$  gas pair for all polymers is shown in Fig. 4. In general, the performance of these polymers is typical of rubbery polymers; however, this type of analysis does provide insight into the effects of the synthetic modifications. Poly[bis-phenoxyphosphazene], **4**, shows the lowest  $O_2$  permeability and selectivity over  $N_2$ . Taken together, polymers **6–8** show a steady increase in permeability while exhibiting an insignificant loss in selectivity. Thus, increasing the alkyl content on the polymers serves to increase both permeability and selectivity for the  $O_2/N_2$  gas pair when compared to the **4**. However, the trend shown for **6–8** does not apply to polymer **5**. Higher selectivity is noted for **5** at the expense of  $O_2$  permeability. Polymer **11** exhibits a trade-off in performance with a loss of permeability and an increase in selectivity with respect to **5**.

 $CO_2/CH_4$  is an industrially relevant gas separation and thus worthy of examination. The highest selectivity polymers were **5** and **11** and both offered increased performance in terms of both higher  $CO_2$  permeability and ideal separation factor as compared to **4**, Fig. 5. The series of **6**–**8** displayed little significant change in separation factor; however, the  $CO_2$  permeability was sequentially increased by the modification of the phenoxy pendant group.

# 4. Conclusion

In this report, a systematic synthetic modification to phenoxysubstituted polyphosphazenes is described along with the effect that this substitution has on physical and chemical properties as well as gas permeation. The attachment of alkyl groups, up to but not including tert-butyl, depresses the glass transition temperature (Tg); which results in an increase in the permeability for a selection of gases. The O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> gas pairs show that increases in permeability, at the expense of selectivity, can be attained through a slight increase in the steric bulk of the alkyl groups. Once the groups become large, as represented by the tert-butyl moiety, some permeability for both O<sub>2</sub> and CO<sub>2</sub> is lost; however, the membranes become more selective. Furthermore, movement of the tert-butyl group farther from the backbone using a flexible ethyleneoxy spacer results in a completely amorphous structure, which is a reflection of the reduced influence of the aromatic moiety and its tert-butyl substituent on the backbone. This synthetic modification fails to provide any significant increase in gas transport performance.

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